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## **Second Test of Base Hydrolysate Decomposition in a 0.04 Gallon Per Minute Scale Reactor**

R.J. Cena, C.B. Thorsness, T. T.Coburn, and B.E. Watkins

### **Abstract**

The Lawrence Livermore National Laboratory (LLNL) has built and operated a pilot plant for processing oil shale using recirculating hot solids. This pilot plant, was adapted in 1993 to demonstrate the feasibility of decomposing base hydrolysate, a mixture of sodium nitrite, sodium formate and other constituents. This material is the waste stream from the base hydrolysis process for destruction of energetic materials, being studied by researchers at Los Alamos National Laboratory (LANL). In the Livermore process, the waste feed is thermally treated in a moving packed bed of ceramic spheres, where constituents in the waste decompose, in the presence of carbon dioxide, to form solid sodium carbonate and a suite of gases including: methane, carbon monoxide, oxygen, nitrogen oxides, ammonia and possibly molecular nitrogen. The ceramic spheres are circulated and heated, providing the energy required for thermal decomposition. In addition to being an energy source, the spheres provide a large surface area for evaporation and decomposition to occur, avoiding sticking and agglomeration of the waste while undergoing processing. This is the second test of base hydrolysate destruction in this reactor.

We performed a one day (2.5 hour) test of the solids recirculation system, with continuous injection of approximately 0.04 gal/min of waste. Gasses from the packed bed reactor were directed through the lift pipe and water was not condensed. Potassium carbonate (0.356 M) was added to the hydrolysate prior to its introduction to the retort. These two points distinguished this run from the first<sup>1</sup>. Continuous on-line gas analysis was invaluable in tracking the progress of the experiment and quantifying the decomposition products. Analyses showed the primary solid product, collected in the lift exit cyclone, was indeed sodium carbonate, as expected. For the reactor condition studied in this test, N<sub>2</sub>O was found to be the primary nitrogen bearing gas species. In the test, approximately equal quantities of ammonia and nitrogen bearing oxide gases were produced (NO, NO<sub>2</sub> and N<sub>2</sub>O). Under proper conditions, this ammonia and NO<sub>x</sub> can be recombined downstream to form N<sub>2</sub> and O<sub>2</sub> as the primary effluent gases. The emissions of nitrogen oxides were not significantly different between the two runs.

## **Introduction**

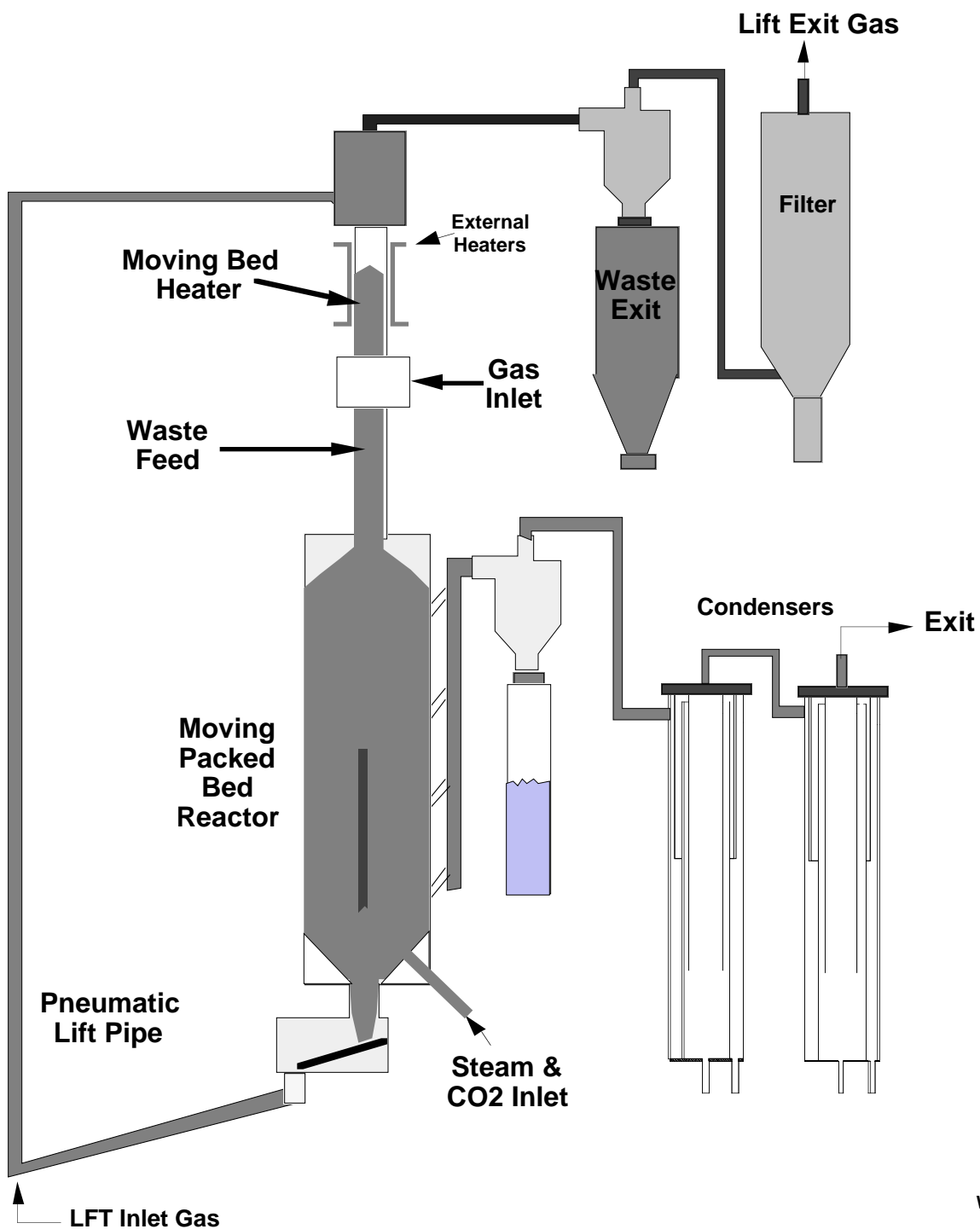
The Lawrence Livermore National Laboratory (LLNL) as part of the Energetic Materials Center, is developing methods for the safe, environmentally sound, destruction of explosives and propellants as a part of the Laboratory's ancillary demilitarization mission. As a result of the ending of the Cold War and the shift in emphasis to a smaller stockpile many weapons, both conventional and nuclear, are scheduled for dismantlement and are being rapidly retired. Energetic materials, both explosives and propellants, from these weapons must either be recycled or safely destroyed. Traditionally, open burn/open detonation has been the method of choice for the destruction of energetic materials. These methods are no longer considered to be environmentally acceptable and we and others are looking for alternative ways to dispose of energetic materials.

The Los Alamos National Laboratory (LANL) has developed a process to demilitarize energetic materials by treatment in boiling aqueous sodium hydroxide. This process is referred to as base hydrolysis and is an excellent way to render these materials non-detonable and non-reactive. However, the base hydrolysis process does produce large volumes hazardous waste that is corrosive and potentially toxic. The base hydrolysate is a mixture of sodium nitrite, sodium formate as well as other, including some unknown, constituents.

Lawrence Livermore National Laboratory has built and operated a pilot plant for processing oil shale using recirculating hot solids. This pilot plant was adapted in the fall and winter of 1993 to demonstrate the feasibility of decomposing base hydrolysate. In the modified LLNL pilot plant, a sample of Los Alamos National Laboratory's base hydrolysate was thermally treated in a moving packed bed of ceramic spheres, where constituents in the waste decompose, in the presence of carbon dioxide, to form solid sodium carbonate and a suite of gases including: methane, carbon monoxide, oxygen, nitrogen oxides, ammonia and possibly molecular nitrogen. The ceramic spheres are circulated and heated, providing the energy required for thermal decomposition. In addition to being an energy source, the spheres provide a large surface area for evaporation and decomposition to occur, avoiding sticking and agglomeration of the waste while undergoing processing. We performed an extended one day test of the solids recirculation system, with continuous injection of approximately 0.04 gal/min of waste for a period of 2.5 hours. Solid sodium carbonate, methane, carbon monoxide, nitrogen oxides were the major products.

## **Pilot Plant Description**

The retort schematic, in Figure 1, shows the configuration of equipment for the waste destruction test. The moving packed bed reactor contains approximately 90 kg of ceramic spheres with an additional 50 kg in the waste feed pipe and 55 kg in



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**Figure 1. Schematic of Hot-Recycled-Solid Pilot Plant for Demonstration of Base Hydrolysate Destruction**

the moving bed heater. The spheres are circulated and maintained at a temperature at or above 550 °C to accomplish the decomposition. The spheres are discharged from the reactor at a rate of approximately 10 kg/min which gives a solids residence time in the reactor of 9 minutes. A gas actuated L-valve meters the spheres from the reactor to the pneumatic lift pipe. The spheres are lifted to the top of the tower and discharged into a gas/solid separator or classifier. The discharge gas passes through a cyclone separator and sintered metal dust filter and is then vented. The spheres, separated from the gas and dust in the classifier are recirculated back to the reactor after passing through a moving packed bed heater. In the reactor, CO<sub>2</sub> is provided as reactants via an injection stinger which dispenses these gases along the centerline. In this test, all produced gas was forced through the reactor to the lift system, exiting with the lift exit gas.

In the previous test<sup>1</sup> reactor gas was passed through a cyclone and then to a two stage condenser to knock out dust and condensables prior to the gas being vented. No significant products were found in the condensed water during that test.

Heat is picked up by the spheres during circulation. The energy is supplied via electric gas heaters, which preheat gas to 700 - 800 °C prior to contacting the spheres and electric heaters strapped to external vessel walls. The combined power input of 8 kW is enough to evaporate and bring to reaction temperature 0.04 gal/min of waste feed.

The primary control of the experiment was to maintain the temperature at the exit of the moving bed reactor at or above 550 °C by adjustment of the waste injection rate. For the test a waste injection rate of 0.04 gal/min was achieved. Figure 3 shows a schematic of the moving bed reactor, with thermocouple positions noted.

### **Base hydrolysate composition**

PBX 9404 (1 pound of PBX /gal. of base) was dissolved in hot 1.5 M sodium hydroxide. The resulting solution (23 kg) contained 30.49 g/L of sodium, 0.89g/L of chloride, 2.88 g/L of nitrate and 13.8g/L of nitrite. It showed a pH of 12.83 and a hydroxide concentration of 285 mM. It also contained an unknown amount of partial hydrolysis products of the HMX. To this solution was added 0.356 mM potassium carbonate. The purpose of adding the additional carbonate was to buffer the system and make the chemical environment within the reactor more similar to that of LLNL's molten salt process<sup>2</sup>.

### **Waste Injection Chronology**

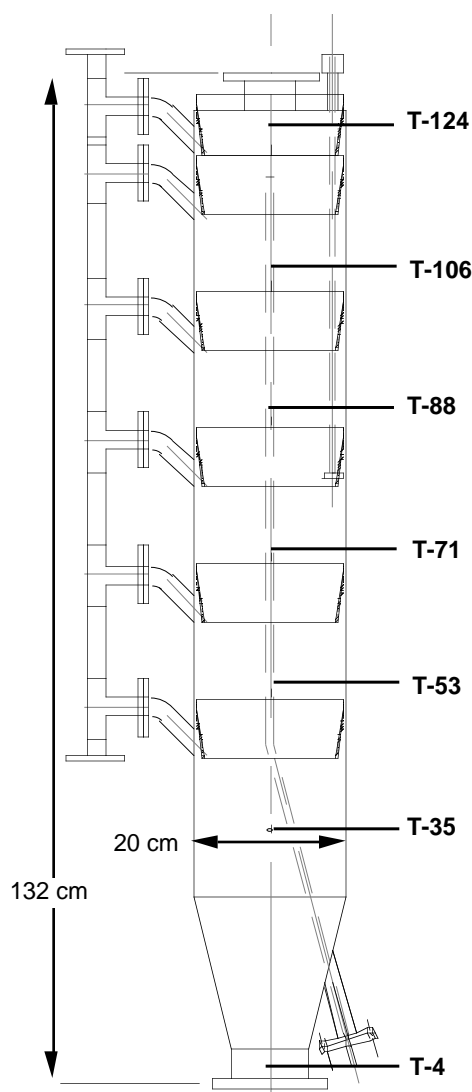
The experiment began at 14:00, with waste injection started at 14:08. Progress of the waste injection was followed using bubblers to record the liquid level in the supply vessel. Figure 3 shows the progress of injection during the experiment, except for the first 30 minutes, where the bubbler was off-line. As shown, the injection continued, at a relatively constant rate for the duration of the test, with the the average waste injection rate over this period being 0.04 gal/min.

## Reactor Temperatures

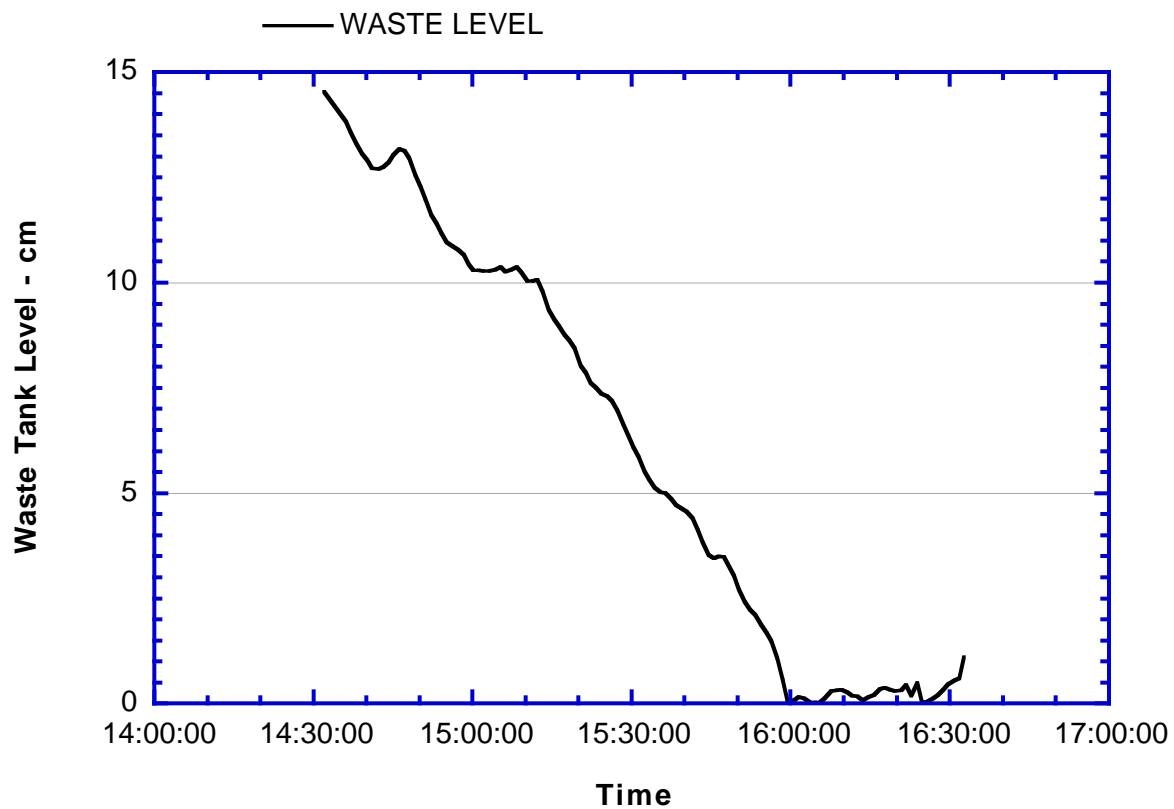
The temperature exiting the moving bed reactor over the course of the runs is shown in Figure 4. As shown, the reactor temperature was at or above 550 °C for the entire period of waste injection.

## Gas Composition

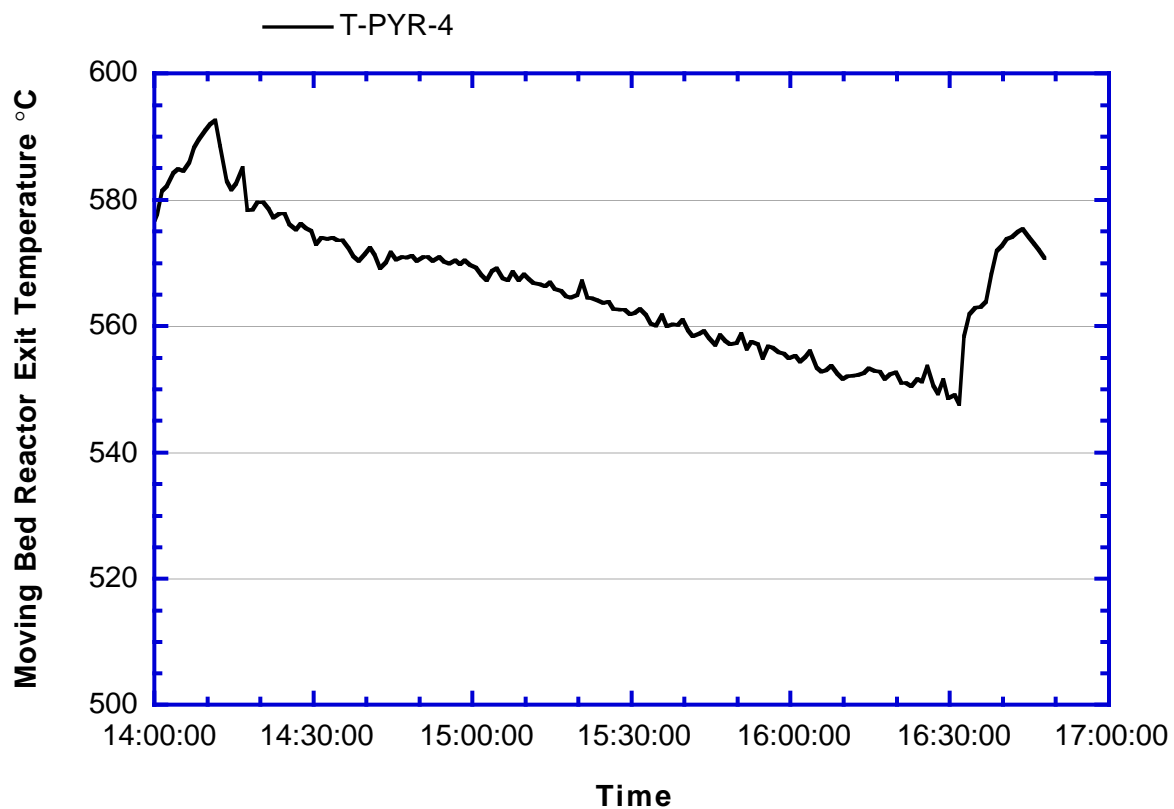
The composition of gas species produced during the base hydrolysate decomposition test was monitored on-line throughout the run. The on-line instruments included a quadrupole mass spectrometer (MS), a fourier transform infrared spectrometer (FTIR), several individual IR meters for CO, CO<sub>2</sub> and NO<sub>x</sub> and an O<sub>2</sub> analyzer. On-line analysis of gas phase components included: NO, NO<sub>2</sub>, N<sub>2</sub>O, O<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O. N<sub>2</sub> levels were dominated by the air and N<sub>2</sub> used as working fluids for pneumatic lifting, pressure balance and L-valve operation. Therefore, N<sub>2</sub> produced from the decomposition of NaNO<sub>2</sub> was not detectable. The gas species of primary interest are the oxides of nitrogen, NO and NO<sub>2</sub> and N<sub>2</sub>O. The FTIR is capable of quantitatively measuring all three of these species and monitored their evolution in the reactor exit gas throughout the test.



**Figure 2. Schematic of Moving Packed Bed Reactor Showing Thermocouple Locations**



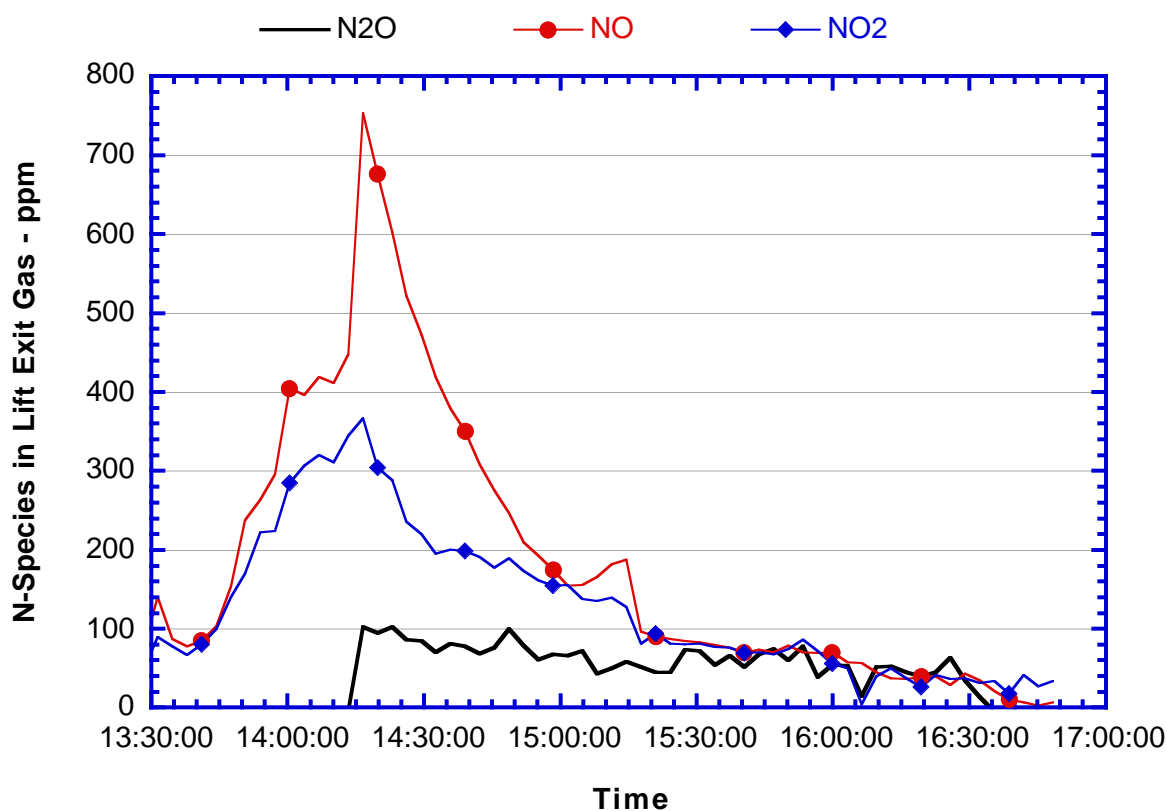
**Figure 3. Waste Injection Tank Level During Test**



**Figure 4. Thermal Response at Bottom of Reactor (T-PYR-4).**



Figure 5 shows the NO, NO<sub>2</sub> and N<sub>2</sub>O production in the lift exit gas during the test as measured by FTIR, in ppm. Figure 6 shows CH<sub>4</sub> and CO concentration in the lift exit gas. Figure 7 shows the three primary lift exit gases, CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>. CO<sub>2</sub> was injected into the reactor at a rate of 45 mMol/s. Finally, H<sub>2</sub>O in the lift exit gas is shown in Figure 8.



**Figure 5. NO, NO<sub>2</sub> and N<sub>2</sub>O in Lift Exit Gas by FTIR Instrument**

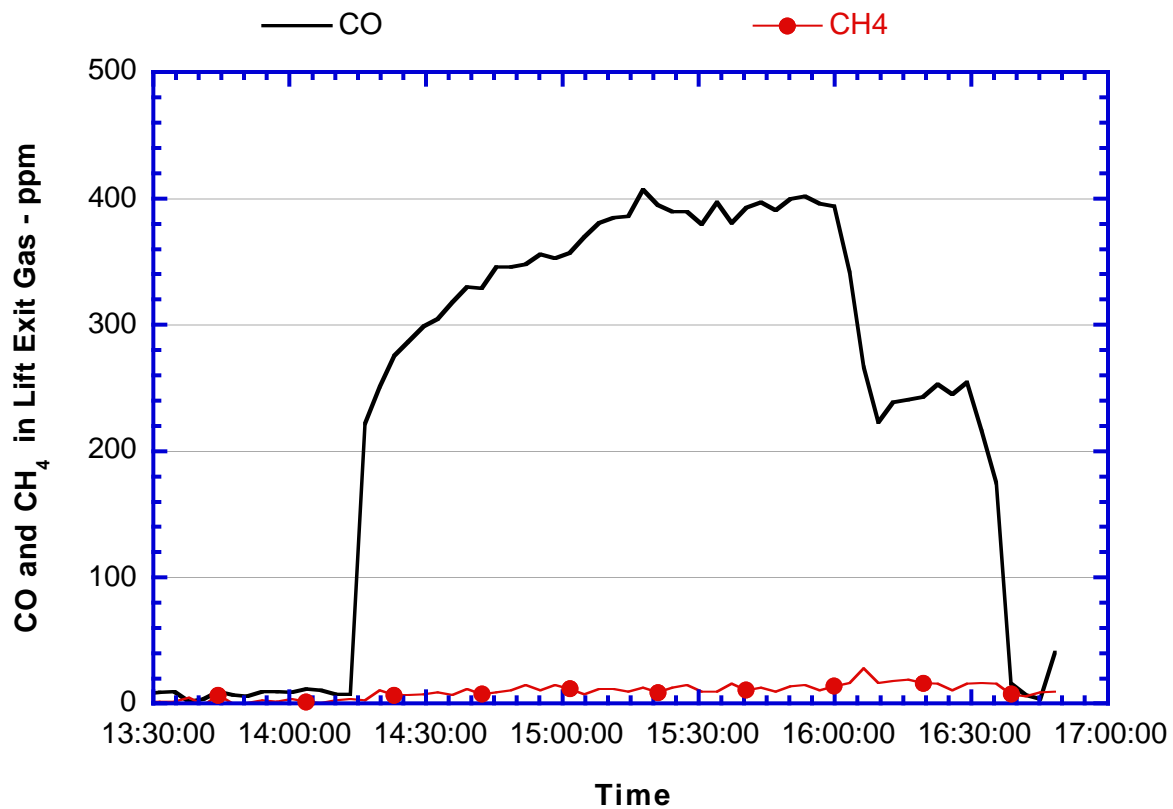


Figure 6. CO and CH<sub>4</sub> in Lift Exit Gas by FTIR Instrument

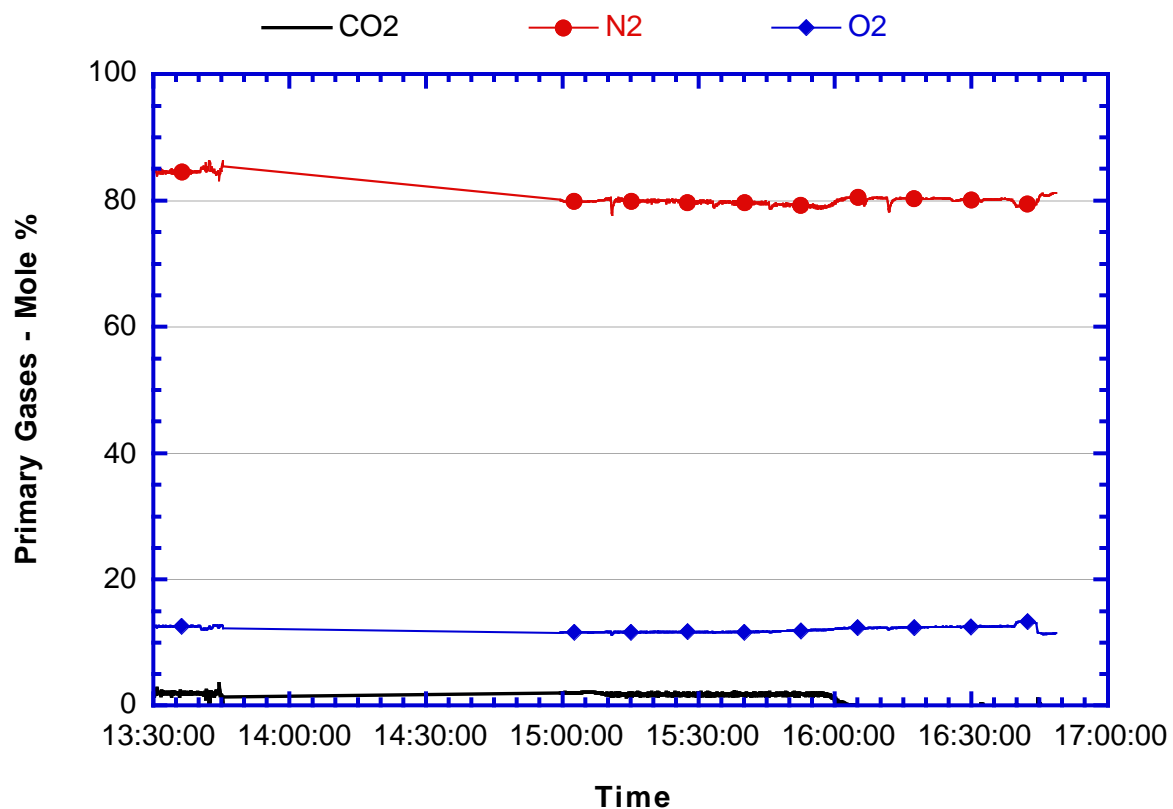
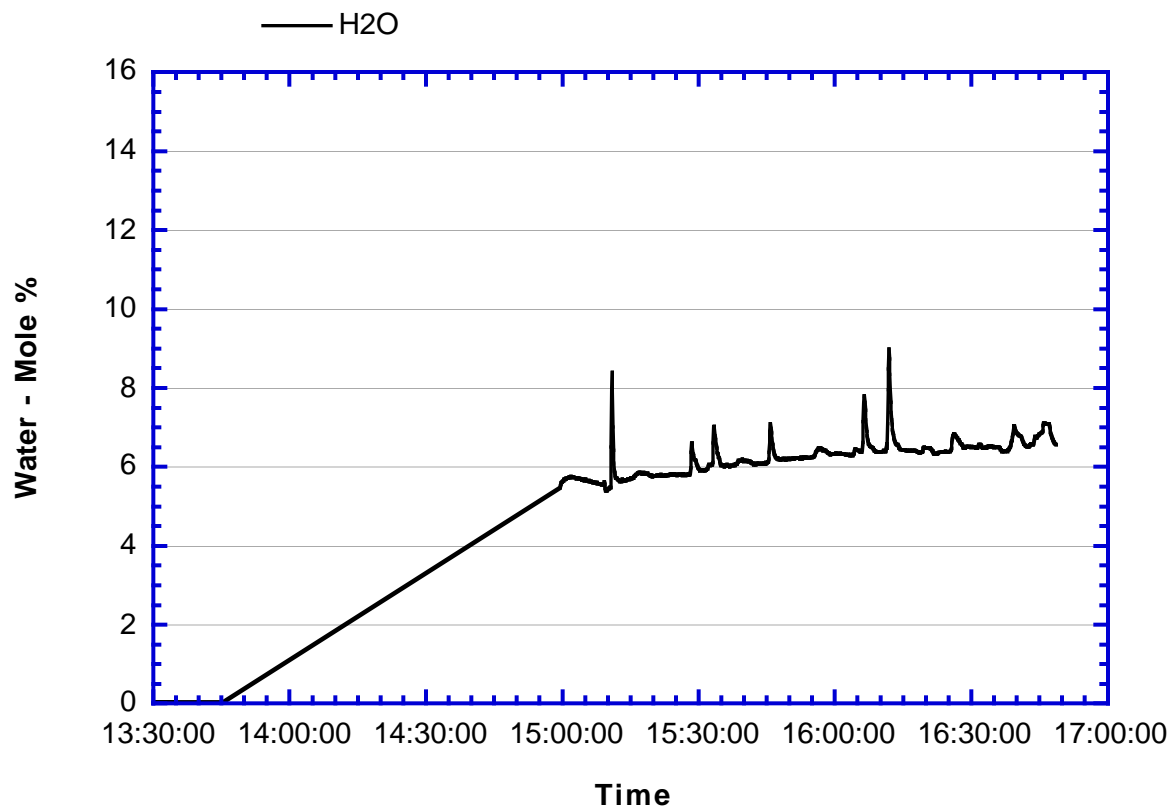
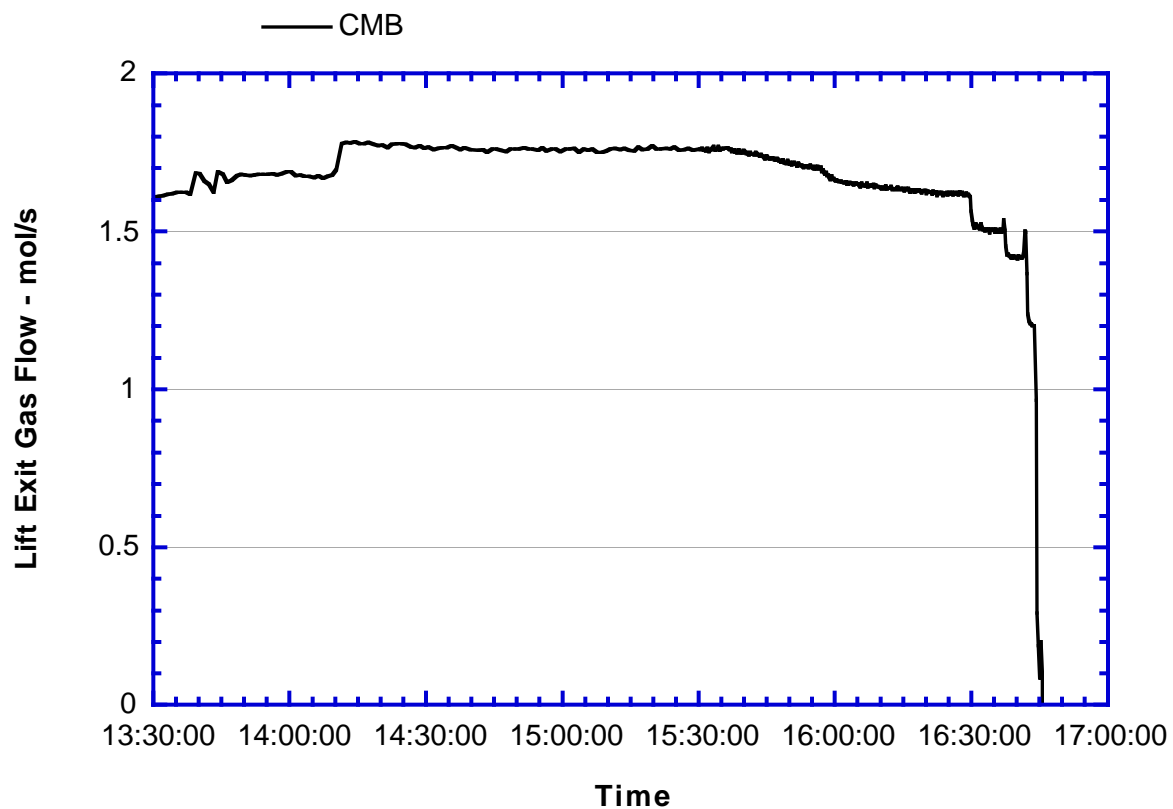


Figure 7. Primary Lift Exit Gases by Mass Spectrometer



**Figure 8. Water in Lift Exit Gas by Mass Spectrometer**



**Figure 9. Lift Exit Gas Flow During Experiment**

## Post Run Sample Analysis and Balances

After final shutdown, we began emptying the vessels of the 171 kg of sphere inventory used. The spheres were removed from the process using the reactor L-valve and during discharge showed no signs of sticking, tacking or agglomeration. The final inventory of the spheres recovered from the process totaled 170 kg, or no net loss of spheres during processing. During the tests, 23.3 kg of base hydrolysate solution was injected, containing a total of 98 grams of nitrogen. Table 1 summarizes the atomic balance for nitrogen for the run. In the table, the high initial concentrations of NO and NO<sub>2</sub> are the result of decomposition of nitrate left on the spheres from a previous experiment. N<sub>2</sub>O was the primary nitrogen oxide produced from base hydrolysate decomposition, and accounts for 15% of the injected nitrogen. To estimate the NO and NO<sub>2</sub> contribution, data from the last 30 minutes of active waste injection was used, corrected for baseline levels, measured following termination of waste injection. Although crude, these values agree pretty well with results of the first base hydrolysate destruction test. The comparison is shown in Table 2.

The total amount of nitrogen produced as nitrogen bearing gases in this test was 23%, compared with 27% measured in the reactor off-gas in the first test. For that test, an additional amount of N<sub>2</sub>O was speculated to have exited in the lift gas, below the detectable limit. However, based on these results, it appears that this may not be the case. Therefore, during base hydrolysate decomposition, approximately 25% of the feed nitrogen has been shown to be released as nitrogen bearing gases.

**Table 1. Nitrogen Balance**

	Concentration	Units	Sample Size	Units	Net N	% of Total
<b>Lift Exit - N<sub>2</sub>O</b>	65	ppm	2.5 & 1.75	hrs & mol/s	14	15%
<b>Lift Exit - NO *</b>	28	ppm	2.5 & 1.75	hrs & mol/s	6	6%
<b>Lift Exit - NO<sub>2</sub> *</b>	8	ppm	2.5 & 1.75	hrs & mol/s	2	2%
<b>Total Measured <sup>ψ</sup></b>				gm	22	23%
<b>Total Injected</b>				gm	98	

\* Data near end of experiment - background      <sup>ψ</sup> Balance is presumed to be Nitrogen

**Table 2. Comparison of N-Species in Exit Gas from Two Tests  
(Percent of Total Nitrogen Injected)**

Test	NO	N <sub>2</sub> O	NO <sub>2</sub>
<b>This Test</b>	6	15	2
<b>1st Test</b>	5	19 - 32 <sup>ψ</sup>	3

<sup>ψ</sup> Depends on N<sub>2</sub>O concentration in Lift

### Conclusions

From the second test of base hydrolysate decomposition, using the Hot-Recycled-Solid (HRS) pilot plant, the following conclusions are drawn:

- **The Hot-Recycle-Solid circulation system operated successfully for 2.5 hours during which 23 kg of base hydrolysate was processed.**
- **The primary solid product was sodium carbonate, which is removed from the system as as fine dust, collected in a gas/solid cyclone separator.**
- **Continuous on-line gas analysis was invaluable in tracking the progress of the experiment and quantifying the decomposition products.**
- **The analyses showed that N<sub>2</sub>O was the major nitrogen oxide species measured in this test. Other experiments in a more oxidizing environment and longer residence times produces NO and NO<sub>2</sub> as the primary nitrogen oxide species.**
- **Ammonia production was equivalent to nitrogen oxide production. The ammonia and NO<sub>x</sub> could be combined in a downstream reactor producing N<sub>2</sub> and O<sub>2</sub> as the primary effluent gases.**
- **Inspection of solids removed from the process following shutdown showed no signs of sticking, tacking or agglomeration.**
- **Addition of Potassium carbonate to the feed has no effect on emmissions**

### References

1. Cena, R.J., Thorsness, C.B., Coburn, T.T. and Watkins, B.E., LLNL Demonstration of Base Hydrolysate Destruction in a 0.1 Gallon Per Minute Scale Reactor, University of California Research Report UCRL-ID-117550.
2. Upadhye, R.S., Watkins, B.E., Pruneda, C.O., and Brummond,, W.A "Molten Salt Destruction as an Alternative to Open Burning of Energetic Material Wastes", presented at the I&EC Special Symposium, American Chemical Society, Atlanta, Georgia, September 19-21, 1994.





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